^{13}C NMR (C_6D_6) δ 177.9 (C=O), 176.3 (C=O), 151.1 (C-5), 140.1 (Ph), 128.9 (Ph), 128.4 (Ph), 127.9 (Ph), 127.4 (Ph), 127.1 (Ph), 126.8 (Ph), 125.5 (Ph), 104.6 (C-1/C-6), 102.4 (C-1/C-6), 85.8, 74.9 (OCH_2Ph), 74.5 (OCH_2Ph), 72.8, 55.0 (OCH_3), 40.4, 40.1, 39.9, 24.1. Exact mass calculated for $C_{32}H_{31}NO_6$ + H: 526.2232, found 526.2275.

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Registry No. **7**, 110519-50-1; **8**, 126257-10-1; **9**, 126257-11-2; **9** aldehyde precursor, 116013-32-2; **10**, 126257-12-3; **10** aldehyde precursor, 126257-20-3; **11**, 126257-13-4; **11** aldehyde precursor, 126373-52-2; **12**, 126373-46-4; **13**, 99371-27-4; **13** 6-*O*-trityl derivative, 126257-19-0; **14**, 126257-14-5; **15**, 126257-15-6; **16**, 126257-16-7; **17**, 110519-52-3; **18**, 126373-47-5; **19**, 126373-48-6; **20a**, 126257-17-8; **20b**, 126257-21-4; **21a**, 126373-49-7; **21b**, 126373-53-3; **22**, 126257-18-9; **23**, 126373-50-0; **24**, 126373-51-1; $Me(Ph)_3P^+Br^-$, 1779-49-3; methyl 2,3-di-*O*-benzyl-β-D-glucopyranoside, 31873-34-4; maleimide, 541-59-3; *N*-phenylmaleimide, 941-69-5.

Supplementary Material Available: Tables of fractional coordinates and temperature factors, bond distances in angstroms, and bond angles in degrees (4 pages). Ordering information is given on any current masthead page.

Synthesis of Fluoro Nitro Ethers by Michael Addition Reactions to Activated β,β-Difluoroolefins

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The ferric chloride catalyzed reaction of isobutyryl chloride with 1,1-difluoroethylene gave 1-chloro-1,1-difluoro-4-methyl-3-pentanone (**1**), which was oxidized with *m*-chloroperbenzoic acid to isopropyl 3-chloro-3,3-difluoropropionate (**2**). β,β-Difluoroolefins 1,1-difluoro-4-methyl-1-penten-3-one (**3**) and isopropyl 3,3-difluoroacrylate (**4**) were prepared by dehydrohalogenation of **1** and **2** with amine bases. Unlike their non-fluorinated analogues, **3** and **4** gave no stable Michael adducts with the salts of nitroalkanes, but with β-nitroalcohols such as 2,2-dinitropropanol (**7**), fluorodinitroethanol (**10**), and 2-fluoro-2-nitropropane-1,3-diol (**13**), the corresponding fluoro nitro ethers were obtained in high yields. Reaction of sodium azide with **1**, **2**, and 2-chloro-2,2-difluoroacetophenone gave 1-azido-1,1-difluoro-4-methyl-3-pentanone (**17**), isopropyl 3-azido-3,3-difluoropropionate (**18**), and 2-azido-2,2-difluoroacetophenone (**19**).

The study of the Michael reactions of β,β-difluorovinyl ketones or acrylic acid derivatatives has been limited because of the inaccessibility of these olefins.[1] Reported synthetic routes to 3,3-difluoroacrylic acid are the zinc-mediated reduction of 2,3-dichloro-3,3-difluoropropionic acid[2] and the reaction of carbon dioxide with (2,2-difluorovinyl)lithium.[3] Although, ethyl 3,3-difluoroacrylate was prepared by cautious dehydrohalogenation of ethyl 3-bromo-3,3-difluoropropionate, dehydrochlorination of the corresponding chloro derivative failed because of disproportionation leading to ethyl 3,3,3-trifluoropropionate.[4] The presence of the β-fluoro groups increased the reactivity of the olefin toward addition of fluoride ion.[1,5]

Nitro-group functionalized ethers are of interest for use in propellant and explosives mixtures.[6] In the case of non-fluorine-containing systems, these ethers cannot generally be synthesized by a base-catalyzed Michael addition of β-nitro alcohols to activated olefins. The explanation for failure of this reaction may be found in the low nucleophilicity of the alkoxide ion[7] and its instability toward the reverse Henry reaction resulting in deformylation.[8] The effect of β-fluoro groups on this addition has not been studied. This report describes a facile synthesis of isopropyl 2,2-difluorovinyl ketone and isopropyl 3,3-difluoroacrylate and some unusual addition reactions of these olefins with nitronate anions and β-nitro alcohols.

Scheme I[a]

$CH_2{=}CF_2 + RCOCl \rightarrow \underset{\mathbf{1}}{CF_2ClCH_2C(O)R}$

$\mathbf{1} + MCPBA \rightarrow \underset{\mathbf{2}}{CF_2ClCH_2C(O)OR}$

$\mathbf{1} + Et_3N \rightarrow \underset{\mathbf{3}}{CF_2{=}CHC(O)R}$

$\mathbf{2} + Et_3N \rightarrow \underset{\mathbf{4}}{CF_2{=}CHC(O)OR}$

[a] R = $CHMe_2$.

Results and Discussion

Synthesis of Isopropyl 3,3-Difluoroacrylate. The Friedel–Crafts acylation of fluoro-substituted ethylenes with acid chlorides has been used to prepare 2-chloro-2-fluoroethyl alkyl ketones.[9] We have extended this method to the ferric chloride catalyzed reaction of isobutyryl chloride with 1,1-difluoroethylene, which gave 1-chloro-1,1-difluoro-4-methyl-3-pentanone (**1**) in 41% yield.

Oxidation of **1** with *m*-chloroperbenzoic acid gave isopropyl 3-chloro-3,3-difluoropropionate (**2**) in 33% yield. Although two products, 2-chloro-2,2-difluoroethyl isobutyrate and **2**, are possible in this oxidation, only **2** was observed. A regiospecific oxidation[10] may have occurred,

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(2) (a) Knunyants, I. L.; Sterlin, R. N.; Bogachev, V. E. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1958**, 425; *Engl. Transl.* **1958**, 407. (b) Dickey, J. B.; McNally, G. U.S. Patent 2,571,678, 1951; *Chem. Abstr.* **1951**, *46*, 4279c.
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(10) A regiospecific reaction was claimed for similar oxidation use for the preparation of 3-fluoroacrylates. See ref 4.

0022-3263/90/1955-3562$02.50/0

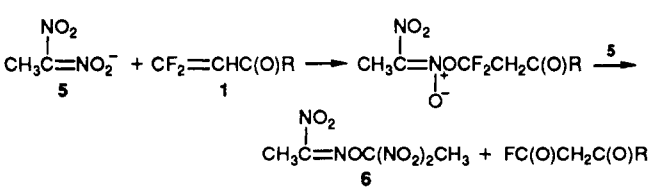
but the possibility that only **2** survived the isolation process cannot be ruled out.

Dehydrochlorination of ketone **1** with triethylamine in diphenyl ether gave 1,1-difluoro-4-methyl-1-penten-3-one (**3**) in 55% yield. Similarly, ester **2** was dehydrochlorinated with triethylamine in methylene chloride to give isopropyl 3,3-difluoroacrylate (**4**) in 49% yield. The dehydrohalogenation reaction was complete in less than 20 min at room temperature. The difluoroolefins **3** and **4** were hydrolytically unstable; when solid sodium carbonate monohydrate was used as a base, chloro difluoro ketone **1** was converted to methyl isopropyl ketone. Dehydrochlorination of cyclohexyl 3-chloro-3,3-difluoropropionate was reported to give an unresolvable mixture of cyclohexyl 3,3,3-trifluoropropionate and cyclohexyl 3,3-difluoroacrylate.[1] The formation of the trifluoromethyl group was not observed in the synthesis of difluoroolefins **3** and **4**.

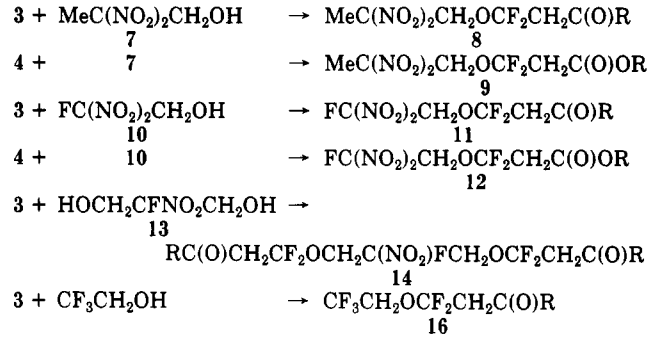
Attempted Michael Reactions with Nitronate Ions. The reaction of the sodium salt of 1,1-dinitroethane (**5**) with unfluorinated methyl vinyl ketone or ethyl acrylate has been reported to give the C-Michael derivatives, 3,3-dinitrobutyl methyl ketone and ethyl 4,4-dinitrovalerate, in high yield.[11] The reactions of difluoroolefins **3** and **4** were studied with 1,1-dinitroethane as a sodium salt or with KF or amine bases in THF, DMSO, DMF, or methylene chloride. Unlike the unfluorinated olefins, **3** and **4** did not give the expected adducts under the conditions studied. Similarly, no adducts were formed from anions of nitroethane or trinitromethane. When the reaction of the dinitro salt **5** and **4** in methylene chloride using collidine as the base was followed by ^{19}F NMR, the appearance of a new absorption at δ −20 (possibly acyl fluoride) was observed. After water was added, the organic layer showed no organic ^{19}F NMR signals, and the dinitro salt **5** was converted to 2,5,5-trinitro-3-aza-4-oxa-2-hexene (**6**) in 85% isolated yield.

Formation of **6** from **5** was reported to occur in the presence of amine catalysts, but the reaction was slow and the yield poor.[12] In a control reaction, without the difluoroolefin **4**, the conversion of **5** to **6** in the presence of collidine in methylene chloride was 15% after 24 h. The reaction of **5** with acetyl chloride was reported to result in acylation of the oxygen of a nitro group to give the mixed nitronic–acetic anhydride, which subsequently gave **6** in high yield.[13]

The failure of nitronate ions to undergo Michael additions with difluoroolefins **3** or **4** may be a result of irreversible addition at the oxygen of the nitro group. In non-fluorinated olefins, such *O*-alkylation occurs rapidly but reversibly to regenerate the nitronate and the olefin. Michael adducts are formed only when the slower and irreversible *C*-alkylation occurs.[11] In the case of these fluoroolefins with decreased electron density at the β-carbon, irreversible *O*-alkylation of the nitro group group would lead to formation of **6**.[14]



Scheme II[a]



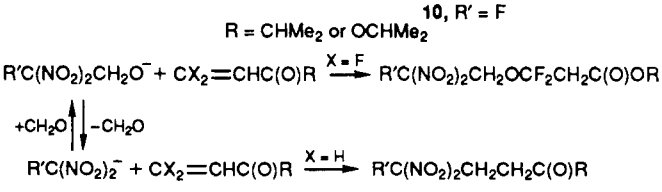
[a] R = $CHMe_2$.

Michael Additions of β-Nitro Alcohols. In contrast to nitronate ions, nitro alcohols underwent Michael addition in the presence of amine bases with difluoroolefins **3** and **4** to give stable fluoro ethers. Reaction of 2,2-dinitropropanol (**7**) with **3** and **4** gave 1,1-difluoro-1-(2,2-dinitropropoxy)-4-methyl-3-pentanone (**8**) and isopropyl 3,3-difluoro-3-(2,2-dinitropropoxy)propionate (**9**) in 72 and 33% yields, respectively. Reaction of 2-fluoro-2,2-dinitroethanol (**10**) similarly gave 1,1-difluoro-1-(2,2-dinitro-2-fluoroethoxy)-4-methyl-3-pentanone (**11**) and isopropyl 3,3-difluoro-3-(2,2-dinitro-2-fluoroethoxy)propionate (**12**) in 82 and 52% yields. Reaction of 2-fluoro-2-nitro-1,3-propanediol (**13**) with **3** gave the diadduct 2,14-dimethyl-8-nitro-5,5,8,11,11-pentafluoro-6,10-dioxapentadecane-3,13-dione (**14**) in 60% yield. No adduct was formed in the reaction of 2,2-dinitro-1,3-propanediol (**15**) with **3** or **4**. Diol **15** has been shown to undergo deformylation under milder conditions than fluoronitrodiol **13**.[15]

Another electronegatively substituted alcohol that was treated with an activated difluoroolefins was trifluoroethanol. Reaction of this alcohol with ketone **3** gave 1,1-difluoro-1-(2,2,2-trifluoroethoxy)-4-methyl-3-pentanone (**16**) in 71% yield.

Because of the instability of **3** and **4**, these difluoroolefins were typically prepared without isolation by reaction of chloro difluoro ketone **1** or ester **2** with triethylamine or collidine in methylene chloride in the presence of an alcohol. When the fluoroolefins were isolated prior to reaction with the nitro alcohols, the yields of the adducts were reduced.

The formation of nitro ethers by Micheal addition of fluorodinitroethanol (**10**) has been observed previously only when the Micheal acceptor was highly polarized as in methyl acetylenecarboxylate.[16] Otherwise, **10** was deformylated in reactions with acrylates to give the corre-



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(14) A reviewer has noted that addition of nitronate ion **5** to olefin **1** may be reversible, but cannot be readily detected because the adduct reacts rapidly by an alternative pathway involving C–F cleavage.
(15) Berkowitz, P. T.; Baum, K. *J. Org. Chem.* **1980**, *45*, 4853.
(16) Grakauskas, V.; Baum, K. *J. Org. Chem.* **1969**, *34*, 3927.
(17) Grakauskas, V. *J. Org. Chem.* **1973**, *38*, 2999.

sponding C-addition products, 3-fluoro-3,3-dinitrobutyrates.[17] Similarly, 7 was deformylated to dinitroethane, which upon Michael addition gave 4,4-dinitrovalerates.[11]

Azido Difluoro Derivatives. The reaction of chloro difluoro ketone 1 or ester 2 with sodium azide at room temperature for 16 h, gave the corresponding azido derivatives 1-azido-1,1-difluoro-4-methyl-3-pentanone (17) and isopropyl 3-azido-3,3-difluoropropionate (18), in 67 and 53% yields.

$$1 + NaN_3 \rightarrow \underset{17}{N_3CF_2CH_2C(O)R}$$

$$2 + NaN_3 \rightarrow \underset{18}{N_3CF_2CH_2C(O)OR}$$

$$R = CHMe_2$$

The mechanism of this reaction was not established but possibly proceeds by an elimination–addition sequence similar to that observed in the disproportionation reaction of cyclohexyl 3-chloro-3,3-difluoropropionate with fluoride ion.[1] Addition of an azide ion to fluoroolefins such as tetrafluoroethylene has been reported,[18] but the direct nucleophilic displacement of chloride in a chloro difluoro group by azide ion has not been reported.[19] Under the conditions employed for the synthesis of azido difluoro compounds 17 and 18, no reaction between 1-chloro-1,1-difluoroacetophenone and sodium azide was observed, but in DMSO at 100 °C, these reactants gave 1-azido-1,1-difluoroacetophenone (19) in 81% yield after 5 min. This reaction may involve nucleophilic displacement of chloride by the azide ion.[20]

$$C_6H_5C(O)CF_2Cl + NaN_3 \rightarrow \underset{19}{C_6H_5C(O)CF_2N_3}$$

Experimental Section[21]

1-Chloro-1,1-difluoro-4-methyl-3-pentanone (1). 1,1-Difluoroethylene gas was passed through a mechanically stirred suspension of anhydrous $FeCl_3$ (200 g, 1.25 mol) in CH_2Cl_2 (1 L) at −10 °C while isobutyryl chloride (106 g, 1.00 mol) was added dropwise. After the addition of the acid chloride was complete, the flow of 1,1-difluoroethylene was continued for an additional 10 min. The mixture was stirred for 1 h at 0 °C and poured onto ice (500 g) and 35% aqueous HCl (250 mL). The organic layer was separated, washed with aqueous HCl (2 × 200 mL), and dried ($MgSO_4$), and the solvent was evaporated. The residue was distilled (65–75 °C/10 mm) to give 70% pure product, and redistillation twice gave 70 g (41%) of 1, bp 68–70 °C (25 mm): IR 3050, 1710 cm^{-1}; ^{1}H NMR δ 1.05 (d, J = 7 Hz, 6 H), 2.7 (m, J = 7 Hz, 1 H), 3.5 (t, J = 12 Hz, 2 H); ^{19}F NMR ($CFCl_2CF_2Cl$) −57.0 (t, J = 12 Hz). Anal. Calcd for $C_6H_9ClF_2O$: C, 42.24; H, 5.30; F, 22.27. Found: C, 42.12; H, 5.51; F, 22.05.

Isopropyl 3-Chloro-3,3-difluoropropionate (2). A solution of 1 (7.5 g, 0.05 mol) and *m*-chloroperbenzoic acid (10 g) in 1,2-dichloroethane (50 mL) was heated at 60 °C for 16 h. The solution was cooled, filtered, and washed with 5% aqueous Na_2CO_3. The organic layer was dried ($MgSO_4$) and distilled to yield 3.0 g (33%) of 2, bp 68–70 °C (10 mm): IR 3000, 1745 cm^{-1}; ^{1}H NMR δ 1.05 (d, J = 7 Hz, 6 H), 3.0 (t, J = 12 Hz, 2 H), 4.8 (m, 1 H); ^{19}F NMR −58.0 (t, J = 12 Hz). Anal. Calcd for $C_6H_9ClF_2O_2$: C, 38.62; H, 4.86; F, 20.36. Found: C, 38.75; H, 4.80; F, 20.10.

1,1-Difluoro-4-methyl-1-penten-3-one (3). A solution of 1 (3.7 g, 0.02 mol) in diphenyl ether (20 mL) was cooled to 10 °C and triethylamine (2.2 g, 0.02 mol) was added dropwise. This mixture was heated at a pot temperature of 105 °C under vacuum (20 mm) and the distillate was collected and redistilled to yield 1.5 g (55%) of 3, bp 40–42 °C (20 mm): IR 3000, 1705 cm^{-1}; ^{1}H NMR δ 1.05 (d, J = 7 Hz, 6 H), 2.5 (m, 1 H), 5.2 (dd, J = 3, 22 Hz, 1 H); ^{19}F NMR −64.2 (dd, J = 3 Hz, 14 Hz, 1 F), −59.0 (dd, J = 14 Hz, 22 Hz, 1 F). Anal. Calcd for $C_6H_8F_2O$: C, 53.73; H, 5.96. Found: C, 53.73; H, 5.73.

Isopropyl 3,3-Difluoroacrylate (4). A solution of 2 (5.5 g, 0.03 mol) and triethylamine (3.0 g, 0.03 mol) in CH_2Cl_2 (50 mL) was stirred 30 min at 25 °C, washed with 10% aqueous HCl (25 mL), dried over ($MgSO_4$), and evaporated. The residue was distilled to give 2.2 g (49%) of 4, bp 43–45 °C (10 mm): IR 3000, 1745 cm^{-1}; ^{1}H NMR δ 1.05 (d, J = 7 Hz, 6 H), 4.7 (m, 1 H), 4.8 (m, 1 H); ^{19}F NMR ($CFCl_2CF_2Cl$) −63.5 (dd, J = 3 Hz, 14 Hz, 1 F), −58.0 (dd, J = 14 Hz, 22 Hz, 1 F). Anal. Calcd for $C_6H_8F_2O_2$: C, 48.00; H, 5.36. Found: C, 47.91; H, 5.33.

1,1-Difluoro-1-(2,2-dinitropropoxy)-4-methyl-3-pentanone (8). A solution of 1 (1.7 g, 0.01 mol), 2,2-dinitropropanol (3.0 g, 0.02 mol), and collidine (1.2 g, 0.01 mol) in CH_2Cl_2 (50 mL) was stirred at 25 °C for 2 h, after which time the starting ketone was completely consumed (^{19}F NMR analysis). The solution was washed with aqueous HCl (2 × 50 mL) and dried ($MgSO_4$), and the solvent was evaporated. The residue was distilled to give 2.6 g (92%) of 8, bp 110–112 °C (0.5 mm): IR 3000, 1710, 1570, 1450 cm^{-1}; ^{1}H NMR δ 1.05 (d, J = 7 Hz, 6 H), 2.2 (s, 3 H), 2.55 (septet, J = 7 Hz, 1 H), 3.2 (t, J = 9 Hz, 2 H), 4.6 (s, 2 H); ^{19}F NMR −71.0 (t, J = 9 Hz). Anal. Calcd for $C_9H_{14}N_2F_2O_6$: C, 38.03; H, 4.96; N, 9.95; F, 13.36. Found: C, 38.16; H, 4.96; N, 9.91; F, 13.37.

Isopropyl 3,3-Difluoro-3-(2,2-dinitropropoxy)propionate (9). Similar reaction of 2 (1.8 g, 0.01 mol), 2,2-dinitropropanol (3.0 g, 0.02 mol), and triethylamine (1.0 g, 0.01 mol) for 16 h gave 0.98 g (33%) of 9, bp 125–128 °C (1.0 mm): IR 3000, 1750, 1575, 1450 cm^{-1}; ^{1}H NMR δ 1.1 (d, J = 7 Hz, 6 H), 2.1 (s, 3 H), 3.0 (t, J = 10 Hz, 2 H), 4.8 (s, 2 H), 5.0 (septet, J = 7 Hz, 1 H); ^{19}F NMR −78.0 (t, J = 10 Hz). Anal. Calcd for $C_9H_{14}N_2F_2O_7$: C, 36.00; H, 4.70; N, 9.30; F, 12.66. Found: C, 35.89; H, 4.62; N, 9.44; F, 12.70.

1,1-Difluoro-1-(2-fluoro-2,2-dinitroethoxy)-4-methyl-3-pentanone (11). Similar reaction of 1 (3.4 g, 0.02 mol), 2-fluoro-2,2-dinitroethanol (3.0 g, 0.02 mol), and collidine (2.8 g, 0.023 mol) for 48 h gave 2.4 g (83%) of 11, bp 104–106 °C (0.5 mm): IR 3000, 1710, 1550, 1460 ^{1}H NMR δ 1.05 (d, J = 7 Hz, 6 H), 2.55 (septet, J = 7 Hz, 1 H), 3.2 (t, J = 14 Hz, 2 H), 4.9 (s, 1 H), 5.1 (d, J = 2 Hz, 1 H); ^{19}F NMR −71.0 (t, J = 14, 2 F), −107.0 (td, J = 9 Hz, 2 Hz, 1 F). Anal. Calcd for $C_8H_{11}N_2F_3O_6$: C, 33.34; H, 3.85; N, 9.72; F, 19.78. Found: C, 33.46; H, 3.81; N, 9.81; F, 19.62.

Isopropyl 3,3-Difluoro-3-(2-fluoro-2,2-dinitroethoxy)-propionate (12). Similar reaction of 2 (1.8 g, 0.01 mol), 2-fluoro-2,2-dinitroethanol (1.5 g, 0.01 mol), and collidine (1.2 g, 0.01 mol) for 24 h gave 1.6 g (53%) of 12, bp 98–100 °C (1 mm): IR 3000, 1760, 1550, 1460 cm^{-1}; ^{1}H NMR δ 1.05 (d, J = 7 Hz, 6 H), 3.2 (t, J = 10 Hz, 2 H), 4.9 (s, 1 H), 5.1 (d, J = 2 Hz, 1 H), 5.1 (septet, J = 7 Hz, 1 H); ^{19}F NMR −71.0 (t, J = 10 Hz, 2 F), −106.0 (triplet of d J = 9 Hz, J = 2 Hz, 1 F). Anal. Calcd for $C_8H_{11}N_2F_3O_7$: C, 31.58; H, 3.65; N, 9.12. Found: C, 31.40; H, 3.80; N, 9.32.

2,14-Dimethyl-8-nitro-5,5,8,11,11-pentafluoro-6,10-dioxapentadecane-3,13-dione (14). Similar reaction of 1 (4.0 g, 0.022 mol), 2-fluoro-2-nitro-1,3-propanediol (1.4 g, 0.01 mol), and collidine (2.4 g, 0.02 mol) for 24 h gave 3.4 g (85%) of 14 as an oil. An analytical sample was prepared by chromatographing the crude oil on silica gel with hexane containing 5% ethyl acetate to give 14, an oil: IR 3000, 1720, 1580, 1460 cm^{-1}; ^{1}H NMR δ 1.0 (d, J = 7 Hz, 12 H), 2.5 (septet, J = 7 Hz, 2 H), 3.0 (t, J = 10 Hz, 4 H), 4.3 (d, J = 16 Hz, 4 H); ^{19}F NMR −71.0 (t, J = 10, 4 F), −133.6 (quint, J = 16 Hz, 1 F). Anal. Calcd for $C_{15}H_{22}NF_5O_6$: C, 44.23; H, 5.58; N, 3.63. Found: C, 44.29; H, 5.67; N, 3.63.

1,1-Difluoro-1-(2,2,2-trifluoroethoxy)-4-methyl-3-pentanone (16). Similar reaction of 1 (3.6 g, 0.02 mol), 2,2,2-trifluoroethanol (6.5 g, 0.06 mol), and 2.8 g (0.023 mol) of collidine (2.8 g, 0.023 mol) in CH_2Cl_2 (50 mL) for 16 h gave 3.3 g (71%)

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(19) Replacement of bromide from a $CBrF_2$ group has been reported by an elimination–addition sequence: Postovoi, S. A.; Zeifman, Y. U.; Knunyants, I. L. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1986**, 1306; *Engl. Transl.* **1986**, 1183.

(20) Krespan, C. G. *J. Org. Chem.* **1978**, *43*, 637.

(21) Explosive properties of the polynitro ethers described below have not been investigated. Adequate safety shielding should be used in all operations. 2-Fluoro-2,2-dinitroethanol is a severe skin irritant and contact should be avoided. IR spectra were recorded in CH_2Cl_2 on a Perkin-Elmer 700 spectrometer. ^{1}H and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Varian T-60 spectrometer and are reported in ppm relative to TMS and $FCCl_3$.

of **16**, bp 55–57 °C (3 mm): IR 3000, 1710 cm^{-1}; ^1H NMR δ 1.0 (d, J = 7 Hz, 6 H), 2.5 (septet, J = 7 Hz, 1 H), 3.0 (t, J = 8 Hz, 2 H), 3.95 (q, J = 8, 2 H); ^{19}F NMR −71.6 (t, J = 8 Hz, 2 F), −74.8 (t, J = 8 Hz, 3 F). Anal. Calcd for $C_8H_{11}F_5O_2$: C, 41.03; H, 4.73; F, 40.57. Found: C, 41.05; H, 4.90; F, 40.68.

1-Azido-1,1-difluoro-4-methyl-3-pentanone (17). A mixture of **1** (1.7 g, 0.01 mol) and sodium azide (0.8 g, 0.011 mol) in acetone (10 mL) was stirred at 25 °C for 1 h, after which time ^{19}F NMR analysis showed the absence of starting ketone. The solvent was evaporated and the residual oil distilled to give 1.2 g (67%) of **17**, bp 30–31 °C (0.5 mm): IR 3000, 2190, 1710 cm^{-1}; ^1H NMR δ 1.0 (d, J = 7 Hz, 6 H), 2.6 (septet, J = 7 Hz, 1 H), 3.1 (t, J = 11 Hz, 2 H); ^{19}F NMR −70.4 (t, J = 11 Hz). Anal. Calcd for $C_6H_9F_2N_3O$: C, 40.67; H, 5.12; N, 23.70. Found: C, 40.57; H, 5.01; N, 23.65.

Isopropyl 3-Azido-3,3-difluoropropionate (18). Similar reaction of **2** (2.0 g, 0.011 mol) and sodium azide (1.2 g, 0.017 mol) for 16 h gave 1.1 g (53%) of **18**, bp 55–58 °C (20 mm): IR 3000, 2190, 1760 cm^{-1}; ^1H NMR δ 1.05 (d, J = 7 Hz, 6 H), 3.0 (t, J = 12 Hz, 2 H), 5.05 (septet, J = 7 Hz, 1 H); ^{19}F NMR −70.4 (t, J = 12 Hz). Anal. Calcd for $C_6H_9F_2N_3O_2$: C, 37.30; H, 4.69; N, 21.75. Found: C, 37.09; H, 4.87; N, 22.06.

2-Azido-2,2-difluoroacetophenone (19). A mixture of chlorodifluoroacetophenone (1.8 g, 0.01 mol) and sodium azide (1.0 g, 0.014 mol) in dimethyl sulfoxide (5 mL) was heated at 100 °C for 5 min and then cooled to ambient temperature and diluted with water (50 mL). The mixture was extracted with CH_2Cl_2 (20 mL) and the organic layer washed with water (2 × 20 mL), dried ($MgSO_4$), and evaporated. The residue was distilled to give 1.5 g (81%) of **19**, bp 75–76 °C (1.0 mm): IR 3050, 2200, 1720 cm^{-1}; ^1H NMR δ 7.0–7.5 (m); ^{19}F NMR −78.4 (s). Anal. Calcd for $C_8H_5F_2N_3O$: C, 48.74; H, 2.56; N, 21.31. Found: C, 48.67; H, 2.81; N, 21.02.

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Additions of Alkyllanthanum Triflates to Carbonyl Compounds: Reactive Organometallic Nucleophiles

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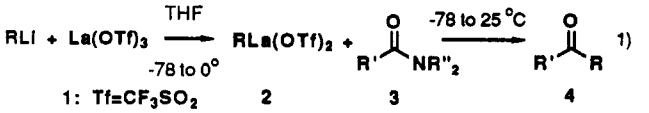
Addition of alkyl- or aryllithium compounds to lanthanum(III) triflate [$La(OSO_2CF_3)_3$, **1**] in ethereal solvents produces the title reagents **2** that undergo nucleophilic addition to carbonyl compounds under mild conditions. These reagents resemble alkylcerium halides in their reactions with enolizable carbonyl compounds but are more reactive. In particular, they are useful for the conversion of hindered, tertiary amides to ketones. ^1H NMR spectroscopy was employed to clarify mechanistic aspects of this addition process. The title reagents actually appear to be a mixture of several species; formulation of their structure has proven elusive. However, in the presence of a tertiary amide, these species react to give a single, tetrahedral intermediate, which is quite stable in solution.

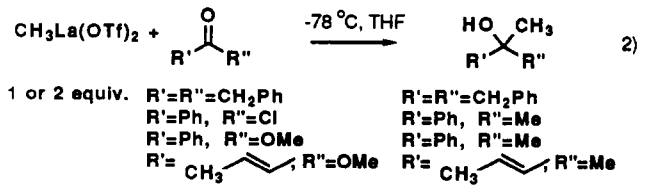
Introduction

There has been considerable recent interest in the chemistry of organolanthanide compounds and their application as reagents for organic synthesis.[2] In particular, organometallic compounds derived from cerium halides and related compounds undergo chemoselective additions to carbonyl compounds, even with easily enolizable systems.[3] We recently discovered that organolanthanum triflates **2**, derived from the reaction of organolithium compounds with lanthanum(III) triflate **1**,[4] undergo smooth addition–elimination reactions with tertiary amides **3** to provide ketones **4** (eq 1).[5] We report here full details of this work and describe further results concerning the reactivity of these reagents.



Results and Discussion

Reactions of $RLa(OTf)_2$ with Carbonyl Compounds. The reactions of reagents **2** with aldehydes and ketones parallel those described for organocerium chlorides ($RCeCl_2$), i.e. enolizable systems such as 1,3-diphenylacetone react cleanly, affording the expected addition product in very high yields (Table I, entry 1, and eq 2).



We do note, however, that reagents **2** appear to be more reactive than organocerium halides; the addition reactions employing **2** are practically complete within minutes of mixing at −78 °C whereas those involving $RCeCl_2$ require

(1) (a) Ontario Postgraduate Scholar, 1989. (b) Watsearch Summer Student.

(2) For a review of the use of organolanthanides in organic synthesis, see: Long, J. R. In *Handbook on the Physics and Chemistry of the Rare Earths*; North Holland Publishing Co.: Amsterdam, 1986; Chapter 57.

(3) For the use of organocerium(III) reagents in synthesis, see: (a) Imamoto, T.; Takiyama, N.; Nakamura, K.; Hatajima, T.; Kamiya, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4392 and references cited therein.

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